



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Preparation of Polychloroprene

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

THIS INVENTION relates to high molecular weight polychloroprene. More particularly this invention relates to a process for preparing high molecular weight polychloroprene which can be greatly extended with portions of oil and to extended oil products.

Polychloroprene has the outstanding ability that it may be advantageously extended with proportions of oils and it has long been used in this way. Higher molecular weight polychloroprene would be even more useful since on the one hand it would make it possible to increase the proportion of oil and thereby reduce the cost of the compound without impairing the properties and, on the other hand, it would make it possible to obtain improved properties while using a formulation of higher molecular weight polychloroprene of the same cost. Still further improvement of properties of polychloroprene would result from higher molecular weight polychloroprene if the oil were omitted.

The polychloroprene produced by the presently available methods has a number-average molecular weight of about 4×10^5 which limits the degree of oil extension of the polymer. These methods do produce very small amounts of higher molecular weight polychloroprene but it is difficult to isolate it from the lower molecular weight polychloroprene and thus such methods are both impractical and uneconomical.

According to one aspect of the present invention we provide a process for polymerising chloroprene in which the polymerisation

is carried out in an alkaline aqueous emulsion at a temperature below 22°C . in the presence of 3×10^{-4} to 4×10^{-4} gram moles per 100 grams of chloroprene of a chain transfer agent, the polymerisation being arrested after 67 to 73 percent of the chloroprene has polymerised whereby a substantially gel free polychloroprene polymer having a number average molecular weight of at least 8×10^5 is obtained.

After removing the unreacted polychloroprene, the aqueous dispersion of the polychloroprene can be blended with a water emulsion containing about 20 to 40 percent by weight of the polychloroprene of hydrocarbon oils of low volatility such as aromatic petroleum oils and then the blended polychloroprene which has been oil extended can be isolated from the aqueous dispersion. Alternatively, the polychloroprene can be isolated from the alkaline aqueous dispersion and then blended with about 20 to 40 percent by weight of the polychloroprene of hydrocarbon oils. A convenient method for isolating the polychloroprene from the alkaline aqueous dispersion either before oil extension or after oil extension in the aqueous emulsion is by acidification and freezing as described in Specification No. 504,466.

The polychloroprenes produced by the process of this invention have very high number average molecular weights, being at least about 800,000. This is twice as high as the number average molecular weight of the highest polychloroprene hitherto made directly by polymerization. Polychloroprenes of molecular weight above 800,000 have up to now been formed only in small proportions (less than 5%) along with polymers of lower molecular weight and had to be isolated by dissolving the mixed high and low polychloroprenes in benzene and precipitating the material of highest molecular weight by controlled addition of methanol.

The high molecular weight polymers of this invention are free from gel polymer, that is,

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they are completely soluble in aromatic hydrocarbon solvents at ordinary temperatures. Prior attempts to polymerize chloroprene to give substantial quantities of high molecular weight, i.e. above 400,000, polymers have been ineffective and often gave gel polymers which were impossible to be readily mixed with oil to give a homogeneous blend by means of available equipment such as Banbury mixers. When the improved process described above is used, the substantially gel-free, soluble polychloroprene of number average molecular weight above about 800,000 is produced in normal 70% yields by the familiar emulsion polymerization techniques such as the process of U.S. patent 2,567,117. The conditions of this improved process are critical and, if these conditions are not met, the product is either too low in molecular weight or contains gel polymers.

Gel is defined and determined in the following manner: approximately 0.5 gram of polymer plus 50.0 cc. of benzene are allowed to stand overnight after which the samples are shaken gently for 1 hour. The gel is allowed to settle or is centrifuged out. Ten (10.0) cc. are removed by a pipette and evaporated by dryness. The percent gel is calculated by difference: $\text{percent gel} = (0.2 \text{ S-P}) \times 100/\text{S}$ where P is the polymer weight found in the evaporation and S is the original weight polymer added to the benzene. If $0.2 \text{ S} = \text{P}$, no gel is present.

Although the high molecular weight polychloroprene prepared by the present invention is of primary importance when extended with hydrocarbon oils of low volatility, these polymers are also useful without oil extension, as shown in the examples. Furthermore, they exhibit outstanding properties when extended with other oils such as selected animal and vegetable glycerides and rosin oils.

The procedure used for carrying out the polymerization and isolation, with the exception of the improvement of this invention, is the well-known alkaline emulsion polymerization in the presence of mercaptans, many forms of which process have often been described in patent and journal literature and are applicable here. Recent variations of the prior art which are applicable to the present invention are (1) the use of emulsifying agents which are largely ammonium soaps, followed by drum drying of the latex at temperatures which decompose these ammonium soaps and thus make a washing step unnecessary (see Specification No. 807,496) and (2) chemically coagulating the latex in thin, continuous sheets suitable for washing and drying.

The preferred chain transfer agent (modifying agent or polymerization regulator) is dodecyl mercaptan when used in the prescribed amounts which equals about 0.06 to 0.08 percent by weight of the mercaptan per 100 grams of chloroprene. Other aliphatic mercaptans, particularly those containing 8 to 18 carbon

atoms, can also be used. The mercaptans can be straight chained or branched, primary, secondary or tertiary; however, the straight chain, primary (i.e. n-dodecyl) mercaptans are preferred. Other chain transfer agents known by one skilled in the art to be effective chain transfer agents such as aromatic disulphides, alkyl xanthogen disulphides, etc. are also useful in the improved process.

When a hydrocarbon oil is used for extending the polychloroprene produced according to the present invention, it should be highly aromatic and of such low volatility as would lead to no substantial loss during processing and in use. The preferred oils have flash points above 400°F. and have 38 to 45% of their carbon atoms in aromatic rings, 13-22% of them in naphthenic rings, and 37-43% in paraffinic chains. Their viscosity at 210°F. (SUS) is 80 to 150 and their viscosity-gravity constant 0.925 to 0.945.

The compounding and curing of the polymers made according to the present invention is along the lines long established for curing the common polychloroprenes except that practical stocks can be obtained with much larger proportions of oils and also of fillers and reinforcing agents such as the carbon blacks and clays.

The oil extended high molecular weight polychloroprenes prepared by this invention are useful for many applications such as electric wire insulation, hose covering and for weather strips used around the windshield of automobiles.

The following examples illustrate the nature of the present invention. Parts are by weight unless otherwise indicated.

EXAMPLE 1

A polychloroprene latex is made by dissolving 3 parts by weight of disproportionated rosin and 0.000371 gram moles (0.075 parts) of n-dodecyl mercaptan in 100 parts of chloroprene, dispersing this by intensive agitation in 108.9 parts of water containing 0.55 parts of sodium hydroxide, 0.40 parts of the sodium salts of sulphonated dinaphthylmethane, and 0.30 parts of sodium sulphite and then polymerizing with efficient cooling at 20°C. This polymerization is initiated by adding a water solution containing 5.6% potassium persulphate and 0.15% of the sodium salt of anthraquinone betasulphonic acid and maintained by adding, as needed, a water solution containing 0.35% potassium persulphate and 0.0175% sodium salt of anthraquinone betasulphonic acid. The polymerization is stopped when 70% of the chloroprene has polymerized, as shown by the density of the partly polymerized emulsion, by adding a toluene solution of 0.028 parts of p-tertiary butyl catechol and 0.028 parts of thiodiphenylamine dispersed in water containing as dispersing agents the sodium salts of dinaphthylmethanesulphonic

- acids and the sodium sulphates of fatty alcohols containing 12 to 14 carbon atoms. The unchanged chloroprene is then removed by steam distillation at reduced pressure. [See 5 U.S. 2,467,769]. The polymer is then isolated from the resulting latex by acidifying to pH 5.6, continuously freezing in thin layers as in Specification No. 504,466, washing and drying. 10 The polychloroprene thus prepared has a Mooney viscosity determined according to ASTM D-927-55 T, using the small rotor at 100°C. of 80 (equivalent to about 150 determined with the usual large rotor). It is soluble in benzene and toluene. Its number average 15 molecular weight is about 800,000.

Examples of other suitable catalyst and arresting agents used in the above process can be found in U.S. Patent No. 2,567,117.

EXAMPLE 2

The polymer of Example 1 is extended 20 with oil by mixing the latex made therein, after removal of the unchanged chloroprene but before acidification, with a water dispersion of an aromatic oil made by agitating 25 100 parts of the oil containing 2 parts of disproportionated rosin in 57.9 parts of water containing 0.14 part of sodium hydroxide and 1.0 part of the above sodium salts of sulphonated dinaphthylmethane. This dispersion is mixed with the latex in the proportions 30 required to give 30 parts of oil per 100 parts of the polychloroprene. The nature of the oil, in terms of the pertinent commonly determined constants, is as follows:

Specific gravity (60°F.)	0.9752
Flash point (°F.)	420
Fire point (°F.)	475
Viscosity (at 100°F.)	3200.0
Viscosity (at 210°F.)	85
Refractive index (at 20°C.)	1.5538
Aniline point (°F.)	122
Volatile loss (22 hrs. at 225°F., %)	0.3
Viscosity-gravity constant	0.925
Distillation range (90%, °F.)	775-895
Carbon atoms in aromatic rings (%)	38
Carbon atoms in naphthenic rings	22
Carbon atoms in paraffin chains	40

- 35 The pH of the mixture is then adjusted to 6.3 and the oil-extended elastomer is isolated as described above for the unextended material of Example 1. The dried product has a Mooney viscosity determined with the usual 40 large rotor (ML) of 85 to 100°C.

Other blending oils of similar characteristics are commercially available.

- The products of Examples 1 and 2 are compared in the following tables with a related 45 polychloroprene representative of those known in the prior art and often extended with moderate or large proportions of oil, made by emulsion polymerization of chloroprene in the presence of 0.14% (0.0007 gram moles) of 50 normal dodecyl mercaptan, at 40°C. In Table I the compounding ingredients, exclusive of extending oil, are 50 parts of semi-reinforcing

carbon black, 1 part of phenyl betanaphthylamine, 4 parts of magnesium oxide, 5 parts of zinc oxide, and 0.7 part of 2-mercaptoimidazole per 100 parts of polychloroprene. The 55 stocks are cured for 30 minutes at 153°C. In Table II all compounds contain per 100 parts of polychloroprene, 0.5 part of stearic acid, 2.0 parts of mixed phenyl betanaphthylamine and N,N'-diphenyl p-phenylene diamine, 4.0 parts of magnesium oxide, 0.5 parts each of petrolatum and microcrystalline paraffins, 5 parts of zinc oxide, 1.0 parts of 2-mercaptoimidazole and 1.0 parts of sulphur 60 along with various amounts of semi-reinforcing carbon black and of the aromatic extending oil described above. The stocks are cured for 30 minutes at 153°C. 65

TABLE I

Stock Number	1	2	3
Polychloroprene: (parts by weight)			
Made in Example 1	100		
Made in Example 2		100*	
Made with 0.14% dodecyl mercaptan (0.0007 gram moles) as in prior art			100
Modulus, 400% elongation	3700	1300	2775
Elongation at break	430	740	410
Tensile strength	3800	3100	2800

* The 30 parts of oil contained in the extended polymer made in Example 2 is not included in this figure.

TABLE II

Stock Number	1	2	3	4
Polychloroprene from Example 2*	100'	100'		
Polychloroprene made with 0.14% dodecyl mercaptan (0.0007 gram moles)			100	100
Oil*	80 ²	110 ²	80	110
Carbon black (SRF)*	130	170	130	170
Modulus, 200% elongation	1500	1400	1500	1420
Elongation at break	340	300	290	270
Tensile strength	2325	1950	2025	1775

* Parts by weight

¹The 30 parts of oil contained in the extended polymer made in Example 2 is not included in this figure

²Includes 30 parts of oil incorporated in Example 2.

5 In Table I, it is shown that a polychloroprene made at 20°C. with 0.000371 gram moles of dodecyl mercaptan and 70% conversion according to the present invention (Example 1) gives very high modulus and tensile strength when compounded and cured without extension with oil (Stock 1), much higher than is given by the polymer made according to the prior art with 0.14% (.0007 gram moles) of dodecyl mercaptan (Stock 3), and that even when the product of Example 1 is blended as in Example 2 with 30% of oil, it gives a

higher tensile strength (Stock 2) than the unextended prior art polymer in Stock 3.

15 In Table II, Stocks 1 and 2 illustrate the compounding of the polychloroprene blend of Example 2 with more oil and with carbon black, giving vulcanizates of good properties in spite of these large additions. In comparison, the prior art polychloroprene of Stocks 3 and 4, similarly compounded, are much inferior in vulcanizate properties, particularly tensile strength.

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EXAMPLE 3

An oil-extended product very similar to that made in Example 2 results when the un-extended polymer made in Example 1 is kneaded in a Banbury mixer with the same proportion of the same aromatic oil and other compounding ingredients used in Example 2 for 8 minutes at 110°C. When compounded and cured like the other materials in Table I, it gives results much like those given by Stock 2 of Table I.

EXAMPLE 4

The polymerization is carried out as in Example 1, except that the catalyst solution added is a 1% solution of potassium ferri-
cyanide in water. In order to avoid a slight greenish discoloration in the isolated polymer, 1.45 parts of a 3% hydrogen peroxide solution is added to the latex after the removal of the unused chloroprene and after acidification.

The polymer is then isolated as in Example 1 and is practically the same as the product of that example.

EXAMPLE 5

The product of Example 4 may be extended with oil, emulsified with somewhat different emulsifiers from those used in Example 2.

100 Parts of the aromatic oil used in Example 2 is dispersed in 55.6 parts of water containing 2.14 parts of the sodium salt of disporportionated rosin and 1.0 part of the sodium salt of sulphonated dinaphthylmethane. This dispersion is then mixed with the polychloroprene latex prepared in Example 4 in such proportions so as to give 30 parts of oil for 100 parts of polychloroprene. The mixture is first treated with 3.47 parts of sodium lauryl sulphate and is then acidified with acetic acid to pH 6.3. The intimate blend of oil and polychloroprene is then isolated by coagulating, washing, and drying as described above in Example 2 and is very similar to the product of Example 2.

WHAT WE CLAIM IS:—

1. A process for polymerising chloroprene in which the polymerisation is carried out in an alkaline aqueous emulsion at a temperature below 22°C. in the presence of 3×10^{-4} to

4×10^{-4} gram moles per 100 grams of chloroprene of a chain transfer agent, the polymerisation being arrested after 67 to 73 percent of the chloroprene has polymerised whereby a substantially gel free polychloroprene polymer having a number average molecular weight of at least 8×10^5 is obtained.

2. A process according to claim 1 in which the chain transfer agent is an aliphatic mercaptan of 8 to 18 carbon atoms.

3. A process according to claim 2 where said chain transfer agent is dodecyl mercaptan.

4. A process for polymerising chloroprene substantially as hereinbefore described.

5. A process for polymerising chloroprene substantially as described in Example 1 or 4.

6. A substantially gel free polychloroprene having a number average molecular weight of at least 8×10^5 prepared by a process as claimed in any of claims 1 to 5.

7. A polychloroprene composition comprising a homogeneous blend of polychloroprene prepared by a process as claimed in any of claims 1 to 5 and 20 to 40% by weight of the polychloroprene of an oil.

8. A polychloroprene composition according to claim 7 in which the oil is an aromatic hydrocarbon oil.

9. A polychloroprene composition comprising a homogeneous blend of polychloroprene prepared by a process as claimed in any of claims 1 to 5 and 20 to 40 percent by weight of the polychloroprene of aromatic oils having a flash point greater than 400°F., a viscosity at 210°F. (SUS) of 80 to 150, a viscosity gravity constant of 0.925 to 0.945, the carbon atoms of said oils being distributed so that 38 to 45 percent are in aromatic rings, 13 to 22 percent are in naphthenic rings and 37 to 43 percent are in paraffinic chains.

10. A polychloroprene composition substantially as hereinbefore described.

11. A polychloroprene composition substantially as described in any of Examples 2, 3 or 5.

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